

A Novel Detector for Gas Chromatography Based on UV Laser-Produced Microplasmas

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The use of UV laser-produced microplasmas for the detection of analyte molecules in the effluent gases of a gas chromatograph is described. The microplasmas are formed when a carbon-containing analyte is present in the carrier gas flow but not in the carrier gas alone. The microplasmas are produced by using the 193-nm output of the ArF excimer laser, with only modest pulse energies (10 mJ) required. Three means for detecting the presence of the microplasmas have been effected and are compared: optogalvanic (plasma electron) detection, photoacoustic (blast wave) detection, and photometric (plasma emission) detection, particularly of electronically excited carbon atoms at 248 nm. The relative responses of these three techniques have been determined for microliter injection of acetylene into the helium flow. Present limits for acetylene with the use of the optogalvanic, photoacoustic, and photometric techniques are 500, 500, and 10 ng, respectively. Optimization of these techniques is expected to improve the detection limits by 2-4 orders of magnitude. The virtues of this detector include the fact that it requires no flame and that it is sensitive to carbon-containing species such as CO and CO₂.

Index Headings: Microplasmas; Detectors; Gas chromatography.

INTRODUCTION

The ability of pulsed lasers to produce microplasmas via laser-induced breakdown has been explored almost since the invention of the laser in the early sixties. The majority of this work has employed infrared (Nd:YAG, CO₂) or visible (ruby) lasers to study the laser-induced breakdown properties of gases^{1,2} and solids.³ One major analytical method which resulted from these studies is that of laser-induced breakdown spectrometry (LIBS).^{4,5} In LIBS, an analyte gas or aerosol is converted into a microplasma and the emission spectrum generated is used for elemental analysis. Only recently have UV lasers been employed to generate microplasmas.⁶⁻⁸ The present article describes the use of UV laser-produced microplasmas for the detection of carbon-containing molecules in the effluent gases of a gas chromatography (GC) capillary column.

A laser-produced microplasma results from the focusing of a high-peak-power laser pulse of sufficient energy into a gaseous sample. The microplasma phenomenon is in evidence by the observation of a visible "spark" of broad-band light accompanied by an audible "pop," or acoustic report. Laser-produced microplasma formation is a complex process that is generally well understood and involves the following steps:¹⁻³ The microplasma is initiated by the presence of free electrons early in the laser pulse. While free electrons may be produced by any means, the usual means of free electron production is via nonresonant multiphoton ionization (MPI) where several photons are absorbed by any atomic or molecular

species within the laser focal volume, resulting in the ionization of the intact species or its fragments. When a free electron interacts with an ion in such a manner that the electron-ion pair may be regarded as a continuum system, the absorption of a photon results in a transition to a higher continuum state of the system. This process, called inverse *bremsstrahlung*, results in an increase of the kinetic energy of the electron. Collisional excitation and ionization occur when the electron acquires enough energy (via inverse *bremsstrahlung*) to ionize any atomic or molecular species through electron impact; the net effect of collisional ionization is the production of an ion and an additional electron. The cascade, or avalanche, ionization which occurs as the free electrons within the laser focal volume repeat the processes of inverse *bremsstrahlung* and collisional ionization results in a high degree of ionization within the microplasma. Once the electron population reaches a certain level ($\sim 10^{15}/\text{cc}$), the electrons become the primary absorbers of the remaining laser pulse, heating the focal volume to a very high temperature.¹

Recent work in our laboratory has shown that lasers operating in the ultraviolet can produce resonant microplasmas whose characteristics are different from those produced via nonresonant MPI.⁶ In particular, the UV-generated microplasmas require considerably less incident laser energy (ILE) for their production, and the energy can be deposited into the microplasma in a more controllable manner than in the nonresonant case. In order to use the UV laser-produced microplasma for the detection of carbon-containing gaseous flows, it is necessary that the microplasma formation occur only in the presence of a carbon-containing molecule, but not in the case of the carrier gas by itself. This condition is met in regular gas chromatography, which uses helium, a high-ionization-potential gas (IP = 24.5 eV), as the carrier, minimizing the possibility of gas ionization. Since most organic molecules have IPs in the seven to ten electron volt range, gas ionization is much easier to achieve in their presence than in the presence of helium alone.

A UV laser-produced microplasma displays three characteristics which may be exploited for its detection. A large fraction of the gas is ionized, resulting in the production of both ions and electrons.¹ The presence of these charged species can be detected with an optogalvanic probe. The blastwave (acoustic report) associated with the microplasma can be detected by using a photoacoustic detector, such as a microphone. The microplasma also emits electromagnetic radiation, which can be detected by photometric means.

Previously, excited and ground electronic state molecular and/or atomic fragments have been observed in

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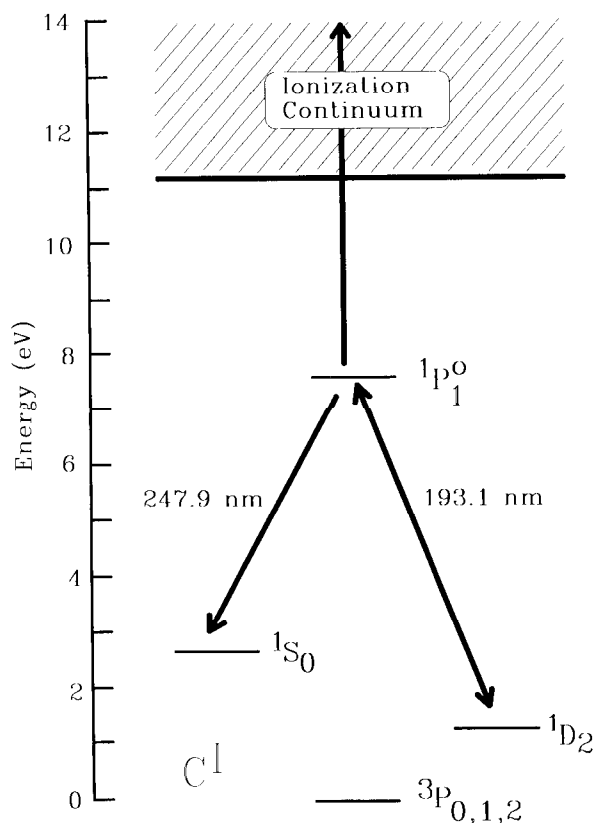


FIG. 1. Partial energy level diagram for carbon atoms.

the laser photolysis (at 193 and 248 nm) of organic,⁹⁻¹¹ organometallic,^{10,12} and organophosphorus^{13,14} species. In particular, the ArF laser-induced atomic carbon $1P_1^o \rightarrow 1S_0$ transition at 248 nm has been used for the photolytic detection of several organic molecules.¹¹ This transition results from a coincident pumping by the ArF laser of the $1D_2$ state of carbon atoms to the $1P_1^o$ state at 193.1 nm (see Fig. 1). This coincidental overlap gives rise to part of the signal at 248 nm that we use for our photometric detection, the remaining being due to plasma atomic emission.

The goal of this paper is to investigate the optogalvanic, photoacoustic, and photometric (248 nm) techniques for the detection of UV laser-produced microplasmas, specifically with the potential development of a new GC microplasma-based detector in mind. For each detection scheme, the linearity of the detector as well as the detection limit for acetylene gas is reported.

EXPERIMENTAL

The experimental apparatus used in this study is detailed below. An ArF excimer laser (Lumonics, model TE 861M-3) supplies the 193-nm pulses (10 pulses per second, 15 ns duration) used to produce the microplasmas. The laser is equipped with unstable resonator optics to give a collimated beam $\frac{1}{8}$ in. \times $\frac{3}{4}$ in. in size. Although the laser is capable of well over 100 mJ pulse energy, for these studies an incident laser pulse energy of only ~ 10 mJ is used. The laser pulse repetition rate of 10 Hz is chosen primarily for convenience, whereas the current limits on repetition rate for commercially available lasers are approaching the 1-kHz range. Even at 10 Hz, the

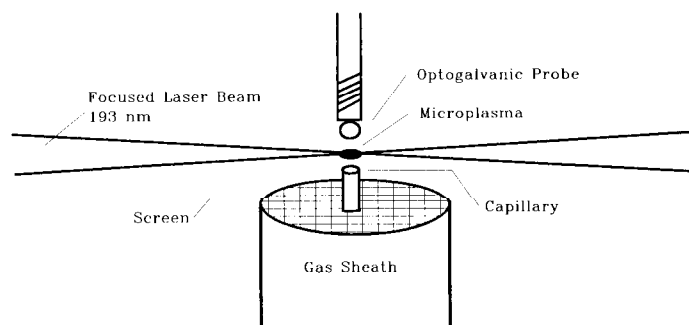


FIG. 2. Enlargement of the capillary/laser focal volume interaction region (capillary diameter = 530 μ m).

capillary peaks of approximately 1 s duration are easily resolved and profiled. The laser pulses are focused through a 1-in.-diameter, 50-mm-focal-length UV grade synthetic fused-silica lens (Melles-Griot). The focus of the beam is directed about 0.5 mm above the tip of a 5-m, 530- μ m-diameter capillary column (Hewlett-Packard), where the microplasma formation takes place. The laser beam is terminated into a 4-in.-diameter volume absorbing calorimeter (Scientech), which also serves to monitor the laser energy.

A blow-up of region around the tip of the capillary column is shown in Fig. 2. The helium carrier gas (Spectra Gases, 99.999%) flows through the capillary column at a rate of about 10 mL/min. The column is surrounded by a $\frac{3}{8}$ -in.-diameter helium sheath (flow rate: 200 mL/min) to prevent the mixing of room gases (especially O_2) with the effluent gas from the capillary. Without this sheath gas and at these flow rates, the entrainment of room air within the effluent gas from the capillary leads to the condition of continuous breakdown, even during the flow of the helium carrier gas alone. The reason for this is that O_2 is easily ionized by the ArF laser due to the absorption of two photons via the intermediate Schumann-Runge bands. The carrier gas is used without further purification while the sheath gas, which consists of tech-grade, oil-free helium, is sent through a series of filters consisting of activated charcoal, molecular sieves, and desiccant. Centering of the column within the sheath is achieved by the use of a wire screen; the screen allows for unrestricted flow of the helium sheath. The helium carrier and sheath both flow into atmospheric pressure.

For determination of the microplasma volume, a small continuous flow of acetylene is directed through the capillary column along with the usual helium carrier. The microplasma is observed under magnification with the use of a microscope, and the dimensions of the microplasma are estimated by visual comparison with the capillary column. The boundaries of the microplasma are fairly well determined by the diameter of the capillary column (530 μ m), with a slight encroachment of the microplasma into the sheath flow due to diffusion of the acetylene. The diameter of the microplasma is determined by the focused laser beam waist and is estimated to be about 50 μ m. The total volume of the microplasma is thus calculated to be approximately 10^{-6} cubic centimeters.

The microplasma is detected via one of three methods. An optogalvanic probe, designed and built by Professor

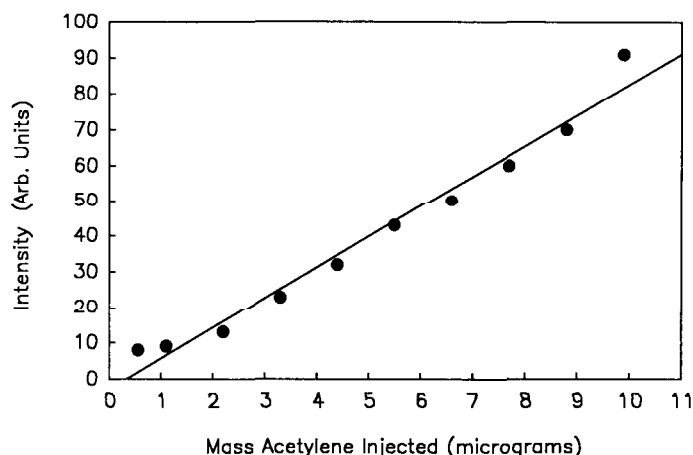


FIG. 3. Signal response as a function of injected C_2H_2 mass for optogalvanic detection.

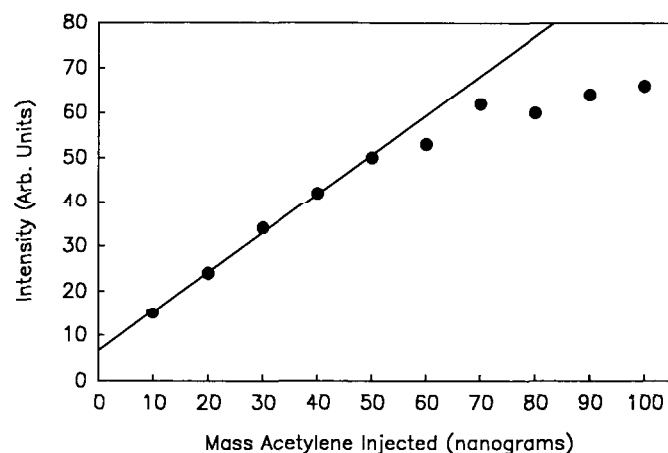


FIG. 4. Signal response as a function of injected C_2H_2 mass for photometric detection.

T. A. Cool,¹⁵ is used to detect free electrons produced within the microplasma. The platinum tip (anode) of the probe is biased to +300 V and is positioned 0.5 mm above the microplasma. The output from the optogalvanic probe is amplified by a differential preamplifier (PAR, Model 113) and then signal averaged with a Stanford Research Systems (SRS) boxcar integrator.

For the second detection scheme, a microphone system (B&K Instruments, Inc., Type 4133 microphone condenser, Type 2615 input stage, and Type 2801 power supply) is employed for photoacoustic detection of the microplasma. The microphone is positioned 1 mm above the microplasma (the closest the microphone can be positioned to the microplasma in order not to clip the laser beam). The signal from the microphone is amplified by a Keithley current amplifier (Model 427) and is then signal averaged with the SRS boxcar.

Photometric detection of the microplasma is employed by monitoring emission of the atomic carbon $^1P_1^o \rightarrow ^1S_0$ transition at 248 nm. A two-lens system (collection efficiency = 1.6%) is used to collect emission from the microplasma and focus it on the entrance slits of a 0.25-m monochromator (McPherson, Model 218) equipped with a Hamamatsu 955R photomultiplier tube (PMT). The signal from the PMT is signal averaged with the SRS boxcar integrator, without prior amplification.

Quantitative samples were prepared by bleeding the sample gas into an evacuated stainless steel manifold equipped with a barocel pressure sensor. The manifold was also equipped with a septum for removing samples. Signal responses for the three detection techniques were measured by injecting a 1–10 μ L sample of acetylene into the helium carrier going into the capillary column.

RESULTS AND DISCUSSION

Figure 3 shows a response plot for the optogalvanic detection scheme in which the mass of acetylene injected into the carrier gas flow is plotted against the signal intensity recorded from the boxcar integrator. The response plot for photoacoustic detection of the acetylene microplasma is very similar to that of the optogalvanic technique. The plot for the photometric detection of acetylene is shown in Fig. 4. The fall-off in the signal

level appears to be due, at least in part, to a drop in the ArF laser intensity over the duration of the experiment. The use of a cryogenic gas processor, not available in our laboratory, would have greatly improved the long-term pulse stability. Sensitivities for the three detection schemes are determined from the response plots and are reported in Table I, along with estimates of potential for improvement for the techniques. One potential advantage of the laser-produced microplasma technique is its sensitivity to noncombustible gases such as CO and CO_2 . The relative detector responses for both of these gases were determined to be within a factor of two of that for acetylene measured under similar conditions with the use of photometric detection at 248 nm.

The relatively poor detection limit observed with the photoacoustic detection scheme is caused by a number of factors. Primary among these is the lack of sufficient sensitivity of the microphone used. Also, the longer response time (tens of microseconds) and the acoustic noise generated by the laser contributed to the low S/N situation. Clearly, increasing the ILE would result in a larger plasma with a corresponding stronger blast wave. Such conditions, however, negate our desire to work with modest laser pulse energies, and, in addition, the ILE can only be increased up to the point where the carrier gas breaks down.

The apparent low sensitivity of the optogalvanic detection scheme is somewhat surprising since even in this small volume the electron population within the microplasma is substantial. One explanation for the lack of sensitivity with the use of our optogalvanic detector is the space charge phenomenon in which the electrons in the outer region of the microplasma repel the core electrons so that most of the electrons are not collected on the small platinum anode bead (1-mm diameter) and are therefore swept away with the carrier gas flow. At the observed detection limit of 500 ng, we estimate that about 10^{11} electrons should be produced (assuming single ionization) from the acetylene molecules which are present within the laser focal volume when the laser fires. The expected peak current from the optogalvanic probe (RC time constant = 20 μ s) resulting from the collection of 10^{11} electrons would be 0.5 mA. This peak current would correspond to 250 mV after being amplified by a factor

TABLE I. Preliminary detector sensitivities for optogalvanic, photoacoustic, and photometric (248 nm) detection schemes for C₂H₂.

Detection scheme	Sensitivity (ng)	Estimated potential for improvement in sensitivity
Optogalvanic	500	High ^a
Photoacoustic	500	Moderate
Photometric	10	Very high ^b

^a By the use of a different electrode configuration.

^b By the use of broad-band detection of microplasma radiation and reduction in rf pickup.

of 10 and terminated into 50 Ω . Taking the sensitivity of the SRS boxcar integrator system to be 5 mV, it is estimated that less than 2% of the electrons produced within the microplasma are being collected. As is indicated in Table I, this problem can be addressed by using a modified electrode configuration, such as parallel plates, to increase the electron collection efficiency.

The sensitivity of the photometric detection technique at 248 nm, while being better than the optogalvanic and photoacoustic techniques by a factor of 50, is still not nearly as high as our estimates indicate it should be. However, our present detection limit, with the use of 10 mJ ILE at 193 nm, indicates a sensitivity similar to LIBS work done on chlorine- and fluorine-bearing molecules, which required 100 mJ ILE at 1064 nm.⁵ Both the photometric and optogalvanic detection techniques are affected by rf pickup from the excimer laser source. This problem is being addressed by shielding the laser better, particularly the power cord, which has been reported to be an rf noise source for older lasers such as ours.¹⁶

CONCLUSIONS

We have demonstrated the viability of the concept of UV laser-produced microplasmas as detectors for carbon-containing effluent gases from a gas chromatograph. Optogalvanic, photoacoustic, and photometric means can be used to detect the presence of a microplasma. It appears that photometric detection of laser-produced mi-

croplasmas deserves further consideration as a detection method for gas chromatography. A two-to-four-order-of-magnitude increase in the sensitivity of the photometric detector should be possible by using broad-band detection of the microplasma instead of the wavelength-specific configuration currently utilized. Studies are underway which include optimization of the microplasma optical detection approach and extension of this technique to other hydrocarbons and halogenated molecules, as well as the detection of fragments other than atomic carbon.

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1. C. Grey Morgan, *Rep. Prog. Phys.* **38**, 621 (1975).
2. D. C. Smith and R. G. Meyerand, Jr., in *Principles of Laser Plasmas*, George Bekefi, Ed. (Wiley, New York, 1976), p. 457.
3. P. K. Carroll and E. T. Kennedy, *Contemp. Phys.* **22**, 61 (1981).
4. L. J. Radziemski, T. R. Loree, D. A. Cremers, and N. M. Hoffman, *Anal. Chem.* **55**, 1246 (1983).
5. D. A. Cremers and L. J. Radziemski, *Anal. Chem.* **55**, 1252 (1983).
6. B. E. Forch and A. W. Miziolek, *Comb. Sci. and Tech.* **52**, 151 (1987).
7. A. Biswas, H. Latifi, L. J. Radziemski, and R. L. Armstrong, *Appl. Opt.* **27**, 2386 (1986).
8. M. Coche, T. Derthoud, P. Mauchien, and P. Camus, *Appl. Spectrosc.* **43**, 646 (1989).
9. J. Schendel, R. Hohmann, and E. L. Wehry, *Appl. Spectrosc.* **41**, 640 (1987).
10. E. L. Wehry, R. Hohmann, J. K. Gates, L. F. Guilbault, P. M. Johnson, J. S. Schendel, and D. A. Radspinner, *Appl. Opt.* **26**, 3559 (1987).
11. R. C. Sausa, A. J. Alfano, and A. W. Miziolek, *Appl. Opt.* **26**, 3588 (1987).
12. J. Schendel and E. L. Wehry, *Anal. Chem.* **60**, 1759 (1988).
13. S. R. Long, R. C. Sausa, and A. W. Miziolek, *Chem. Phys. Lett.* **117**, 505 (1985).
14. R. C. Sausa, A. W. Miziolek, and S. R. Long, *J. Phys. Chem.* **90**, 3994 (1986).
15. P. J. H. Tjossem and T. A. Cool, *Chem. Phys. Lett.* **100**, 479 (1983).
16. C. N. Merrow, private communication.